

\_\_\_\_\_

(12) Publication of Unexamined Patent Application (A)

(11) Japanese Patent Application Disclosure Number: S60-43485

(43) Disclosure Date: March 8, 1985

(51) Int. Cl. <sup>4</sup>	Identification Code	JPO File No.
----------------------------	---------------------	--------------

C 23 C 16/24 8218-4K

Request for Examination: Not requested      Number of Inventions: 1      (5 pages total)

(54) Title of the Invention: Method for Forming Amorphous Silicon Film

(21) Application Number: S58-150328

(22) Filing Date: August 19, 1983

(72) Inventor: Yoshinori Ashida  
1674 Shitami, Nishijo-cho, Higashi-hiroshima-shi

(72) Inventor: Masataka Hirose  
6-4-401 Shirashima Nakamachi, Naka-ku, Hiroshima-shi

(72) Inventor: Kazuyoshi Isogaya  
2-18-15-314 Takada Toshima-ku, Tokyo

(72) Inventor: Nobuhisa Kitagawa  
1-33-27 Hamadayama, Suginami-ku, Tokyo

(71) Applicant: Mitsui Toatsu Chemicals Inc.  
3-2-5 Kasumigaseki, Chiyoda-ku, Tokyo

## SPECIFICATION

### 1. Title of the Invention

Method for Forming Amorphous Silicon Film

### 2. Claims

(1) A method for forming an amorphous silicon film at high-speed and low temperature, characterized by the fact that, in the thermal decomposition of a higher silane gas represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents an integer of at least 2) and the deposition of amorphous silicon on substrate, a group III compound is blended with said higher silane gas.

### 3. Detailed Description of the Invention

The present invention relates to a method of forming an amorphous silicon film at high-speed and low temperature, characterized by the fact that, in the thermal decomposition of a higher silane gas represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents an integer of at least 2) and the deposition of amorphous silicon on substrate, a group III compound is blended with said higher silane gas.

Amorphous silicon films (hereinafter abbreviated as "a-Si films") have excellent photovoltaic characteristics and therefore are commonly used in solar power cells, electrophotographic photosensitive materials and the like. Methods of forming such a-Si films include plasma CVD (Chemical Vapor Deposition) methods which use plasma, using a silicon gas such as monosilane, thermal CVD methods which use thermal decomposition of a silane-type gas, as well as sputtering and other methods. Generally, plasma CVD methods are used, but since these methods require complex equipment and there are numerous manufacturing conditions, the analysis of manufacture is difficult, reproducibility is low, and there are other problems such as ion damage. On the other hand, the chemical CVD method is characterized as being a manufacturing method in which the equipment is simple and inexpensive and reproducibility is high. Nevertheless, since the temperature used in thermal CVD methods using monosilane gas is high at 600°C or above, the quality of the a-Si film obtained is poor, and there are problems such as the fact that an a-Si film cannot be formed on an inexpensive substrate such as glass.

The present inventors, as a result of intensive studies in light of the foregoing problems, invented a method whereby an a-Si film can be formed at low temperature and high speed by using a higher silane instead of monosilane, which has been traditionally used, as a source gas, and the blending and simultaneous thermal decomposition of a group III compound in thermal decomposition.

Specifically, the present invention can be summarized as being a method of forming an amorphous silicon film at high speed and low temperature, characterized by the fact that, in the thermal decomposition of a higher silane gas represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents an integer of at least 2) and the deposition of amorphous silicon on substrate, a group III compound is blended with said higher silane gas.

Present invention is explained below in further detail.

The term "higher silane" as used in the present invention refers to disilane, trisilane, tetrasilane, pentasilane, and the like represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents an integer of at least 2), but from the standpoint of ease of handling substances which are gases at room temperature, such as disilane, trisilane, and tetrasilane, are desirable. These may be used alone or in blends. When used in blends, it does not matter if small amounts of monosilane are also contained.

The term "group III compound" that is used here refers to a hydride or halide, or like compound, of boron (B), aluminum (Al), gallium (Ga), or indium (In), or an organic compound thereof. For example, with respect to boron,  $\text{B}_2\text{H}_{[\text{illegible}]}$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_9$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{10}$ ,  $\text{B}_{10}\text{H}_{14}$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{BI}_3$ ,  $\text{B}_2\text{Cl}_4$ ,  $\text{B}_2\text{Br}_4$ ,  $\text{B}_2\text{I}_4$ ,  $\text{BR}_3$ ,  $\text{BHR}_2$ ,  $\text{BH}_2\text{R}$ ,  $\text{RB}_2\text{H}_5$ ,  $\text{R}_2\text{B}_2\text{H}_4$ ,  $\text{R}_3\text{B}_2\text{H}_3$ ,  $\text{R}_4\text{B}_2\text{H}_2$ , (where  $R$  represents a methyl, ethyl, n-propyl, i-propyl or other lower alkyl group) or  $\text{Al}(\text{BH}_4)_3$  or the like, may be cited.

With regard to aluminum,  $(\text{AlH}_3)_x$ ,  $\text{Li}(\text{AlH}_4)$ ,  $\text{AlF}_3$ ,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{AlI}_3$ ,  $[(\text{CH}_3)_2\text{AlCl}]_2$ ,  $[(\text{CH}_3)_2\text{AlBr}]_2$ ,  $[(\text{C}_2\text{H}_5)_2\text{AlCl}]_2$ ,  $[(\text{C}_2\text{H}_5)_2\text{AlI}]_2$ ,  $[\text{CH}_3\text{AlCl}_2]_2$ ,  $\text{R}_3\text{Al}$  (where  $R$  represents a methyl, ethyl, n-propyl, i-propyl or other lower alkyl group) can be cited.

The amount of group III compound added is:

$$1 \times 10^{-10} \leq \text{X/Si}$$

(Here,  $X$  represents the amount of the aforesaid group III atoms in the group III compound)

introduced into the thermal decomposition system, and Si represents the amount of silicon atoms in the higher silane gas.)

By adding the foregoing amount or more of a group III compound, temperature reduction and speed increase are possible, and the rate of deposition increases with the amount added. However, since the deposited a-Si film becomes a P-type a-Si film, in order to obtain an a-Si film which is extremely close to intrinsic, a range of  $1 \times 10^{-10} \leq X/Si \leq 1 \times 10^{-4}$  is most desirable. Nevertheless, if additional amounts of group III compound are added, then a P-type a-Si film can be deposited at a low temperature and high speed.

With regard to the pressure in the present invention, reduced pressure, normal pressure, or pressure greater than atmospheric pressure may be used. If thermal decomposition is performed at a pressure greater than atmospheric pressure, the film deposition rate increases. In this case, although the purposes of the present invention can be sufficiently achieved in a pressure range of 2 kg/cm<sup>2</sup> G or less, of course operation under a greater pressure presents no problems.

The thermal decomposition temperature in the present invention is 100°C to 600°C, preferably a range of 150 to 500°C. If the decomposition temperature exceeds 600°C, an a-Si film having satisfactory characteristics cannot be obtained.

As a device for implementing the present invention, for example, one like that shown in Figure 1 may be used. 10 indicates decomposition oven (reactor), which is a quartz glass tube of 10 mm  $\phi \times$  500 mm to 60 mm  $\phi \times$  1,000 mm. This may also be angled instead of tubular and is not subject to any special restrictions with respect to form. The reactor is provided with a heater 20 such as a halogen lamp on its outer periphery. The portion inside the tube corresponding to the heater is the decomposition zone, where a silicon susceptor 30 (holder) (a black body which absorbs lamp light is desirable, and a SiC-coated graphite may also be used) and a substrate 40 made of quartz glass, silicon, sapphire, stainless-steel, or the like on which the aforesaid susceptor is placed are set. The temperature of the decomposition zone is measured by means of a thermocouple 45. The end of the reactor is the source gas feeding part 50, which is connected to feeding tubes for the higher silane gas 60, carrier gas 70, and group III compound 80. 61, 71, and 81 are valves, and 63, 73, and 83 are gas flow meters. The other end of the reactor is an exhaust gas outlet port 90. Naturally, the heater need not be a lamp type heater 20, and a resistance keying system which heats the entire

reactor may also be used.

Next, the decomposition operation is explained.

After the decomposition oven has been heated to decomposition temperature or above, inert gas has been introduced and the baking operation performed, the temperature is lowered to the desired decomposition temperature and stabilized.

Next, 100% higher silane or a higher silane which has been diluted with an inert gas such as  $N_2$ ,  $H_2$ , He, or Ar and a group III compound (this too may be 100% concentration or diluted with an inert gas or the like) are simultaneously introduced into the decomposition oven, thermal decomposition is performed, and an a-Si film is deposited on the substrate.

The present invention is explained below by means of Examples of Embodiment.

#### Example of Embodiment 1

A test device like that shown in Figure 1 was used. At the same time as 500 cc/min 1%  $Si_2H_6$  diluted with Ar and 50 cc/min 1ppm  $B_2H_6$  (diluted with  $H_2$ ), 500 cc/min Ar was introduced as a carrier gas into the decomposition oven at 300°C under normal pressure, thermal decomposition was performed, and an a-Si film was deposited on the substrate.

The results are shown in Table 1.

#### Examples of Embodiment 2-4

Tests were performed in the same way as in Example of Embodiment 1 under the conditions shown in Table 1. The results are shown in Table 1.

#### Comparative Examples 1-3

Tests were carried out under the conditions shown in Table 2 in the same way as in Example of Embodiment 1. Results are shown in Table 2.

Table 1 (Examples of Embodiment)

Example of Embodiment	Film formation conditions				Film deposition rate (Å/min)	Film characteristics			
	Higher silane	Group III compound	B/Si	Thermal decomposition temperature (°C)		Dark electrical conductivity ( $\Omega^{[illegible]} cm^{-1}$ )	Photovoltaic conductivity $\rightarrow$ ( $\Omega^{[illegible]} cm^{-1}$ )	Conductivity activation energy (eV)	Optical band gap (eV)
1	Si <sub>2</sub> H <sub>6</sub>	B <sub>2</sub> H <sub>6[illegible]</sub>	1×10 <sup>-5</sup>	300	1,000	2×10 <sup>-10</sup>	5×10 <sup>-3</sup>	0.79	1.62
2	Si <sub>2</sub> H <sub>6</sub>	B <sub>2</sub> H <sub>6[illegible]</sub>	1×10 <sup>-5</sup>	300	600	5×10 <sup>-17</sup>	8×10 <sup>-5</sup>	0.80	1.65
3	Si <sub>3</sub> H <sub>8</sub>	B <sub>2</sub> H <sub>6[illegible]</sub>	1×10 <sup>-10</sup>	200	1,500	3×10 <sup>-10</sup>	1×10 <sup>-6</sup>	0.76	1.64
4	Si <sub>2</sub> H <sub>6[illegible]</sub>	BF <sub>3</sub>	1×10 <sup>-4</sup>	300	800	8×10 <sup>-10</sup>	2×10 <sup>-6</sup>	0.77	1.58

— Under 100 mW/cm<sup>2</sup> irradiation

Table 2 (Examples of Embodiment)

Example of Embodiment	Film formation conditions				Film deposition rate	Film characteristics			
	Higher silane	Group III compound	B/Si	Thermal decomposition temperature (°C)		Dark electrical conductivity ( $\Omega^{-1}cm^{-1}$ )	Photovoltaic conductivity ( $\Omega^{-1}cm^{-1}$ )	Conductivity activation energy (eV)	Optical band gap (eV)
1	SiH <sub>4</sub>	B <sub>2</sub> H <sub>6</sub>	4×10 <sup>-6</sup>	200	— (←→)	—	—	—	—
2	Si <sub>2</sub> H <sub>[illegible]</sub>	—	0	300	30	6×10 <sup>-10</sup>	2×10 <sup>-5</sup>	0.75	1.55
3	Si <sub>3</sub> H <sub>8</sub>	—	0	300	90	2×10 <sup>-10</sup>	1×10 <sup>-6</sup>	0.80	1.62

— Film was not deposited at 1 hr.

#### 4. Brief Explanation of the Drawings

Figure 1 is a diagram explaining the device used to implement the present invention.

Applicant: Mitsui Toatsu Chemicals, Inc.

Figure 1